

FINAL REPORT FOR AOARD PROJECT

Project Title

*Nanoscale Ordering of Functional Materials by Guided Self-Assembly
for Photovoltaic Application: Synthesis and Characterizations*

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CONTENTS

1. Objective of Research	-----	4
2. Description and Background of Research	-----	4
3. Research Contents and Results	-----	5
4. Publication and Presentation	-----	8
5. Paper (1-11) and Presentation Materials	-----	8

1. Objective of Research

- Design, synthesis and characterization of nanoscale-ordered carbon nanotubes and C₆₀ with high photoconductivity
- Study of possibility for adoption of the resulting materials to photovoltaic applications

2. Description and Background of Research

Organic thin films and nanostructures have attracted increasing interest for their potential applications in a variety of advanced technologies, including nonlinear optics (NLO), microelectronics, nanotechnology, light emitting devices, field-effect transistors, liquid crystals, sensors, and photovoltaic solar cells etc. For many of these applications, the devices performance is crucially dependent on the ordering and concentration of the functional molecules in the film or the nanostructure. In contrast to ultra-thin films made by molecular beam epitaxy or chemical vapor deposition, self-assembled monolayers (SAMs) are well ordered and oriented in a comparatively pre-determined way. The SAMs of alkanethiols on Au(111) surfaces have been extensively investigated in terms of the specific structural features on a molecular level, the effect of changes on the molecular backbone, the end group on the SAM structure, and the structural phase diagram as a function of temperature and coverage. Recently, more complex structures such as multi-component SAMs, laterally structured SAMs, surface reactions and heterostructures have attracted a lot of attention due to their pattern features and functional properties. In particular, heterostructures combining SAMs as building templates with polymers, biomolecules, inorganic crystals and nanoparticles, and π -conjugated molecules have provided many potential applications in “brush-like” coating, biosensing, electronics and photonics. However, it is highly desirable to achieve heterostructured SAMs with high stability and nanoscale features in order to study the mechanisms for molecular electronics, organic/polymer photovoltaics and molecular recognition.

Also, electron accepting materials such as C₆₀ and single-wall carbon nanotube (SWNT) in studying photoconducting devices using conjugated polymers have been utilized in some of the past studies. SWNT is a fascinating material due to its characteristic physical properties. Envisioned as a rolled up graphene sheet capped with fullerene like structures, it becomes a metal or a semiconductor as a function of the wrapping angle of the sheet and diameter of the nanotube. In the metallic state, SWNT is a good ballistic conductor with a supported current density at least an order of magnitude higher than that in copper wires of the same diameter. Because of its good mechanical property, high elastic modulus and high optical transparency, SWNT has been used in constructing large area transmissive films, making it an ideal component for electrical coupling in futuristic photonic devices. The thrust of the current

study is to investigate the photodetection efficiency of a polymeric nanocomposite well sequestered with the IR active PbSe QDs and conducting SWNT, both being chemically attached to each other by a novel procedure. PbSe QDs, endowed with a large Bohr radius, exhibit excellent quantum size effects, and can be tuned to a precisely targeted wavelength of absorption in the IR region. Therefore, a stable SWNT-PbSe conjugate by chemical bonding of both components can be a promising candidate for efficient optoelectronic behavior.

3. Research Contents and Results

3.1. System I

For an efficient charge transfer, it is desirable that PbSe QDs are attached on the surface of SWNT intimately and in high concentration. As shown in Figure 1, this has been achieved by a novel procedure of first thiolating the SWNT surface before coupling PbSe QDs. We find that introduction of a thiol functional group on the SWNT surface allows surface adsorption of PbSe QDs at a density significantly higher than that reported in the literature.^[15] For this purpose, the SWNT is first carboxylated and later thiolated by binding a bi-linker molecule 2-aminoethanethiol through an amide bond. The SWNT-COOH activated by *N*-(3-dimethylaminopropyl)-*N*-ethylcarbodiimide hydrochloride (EDAC), easily allows nucleophilic attack of the amine group of 2-aminoethanethiol forming an amide bond as well as resulting in a terminal thiol group on SWNT (SWNT-SH). The attachment between SWNT-SH and PbSe QDs is maximized without compromising its colloidal stability and thus ensuring its homogeneous sequestration in the polymer.

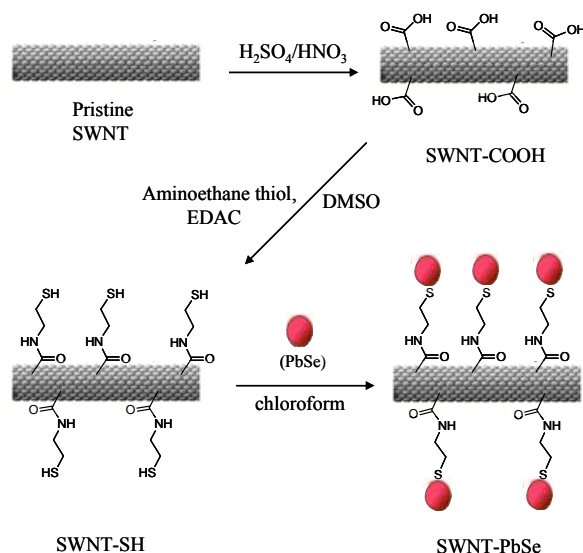


Figure 1. Synthetic route for SWNT coupled with PbSe.

The PbSe QDs (~ 4 nm) used to prepare the conjugate are extremely monodispersed

(Figure 2a) which orient into an ordered hexagonal superlattice when their surface is hydrophobic. Examination of TEM of the SWNT-PbSe conjugate (Figure 2b) reveals that the PbSe QDs bind to the terminal –SH group of the SWNT well in copious population. Figures 2c, 2d and 2e show a zoom of a single SWNT-PbSe conjugate where single strands of SWNT in the SWNT bundles as well as the lattice fringes of PbSe are discernible.

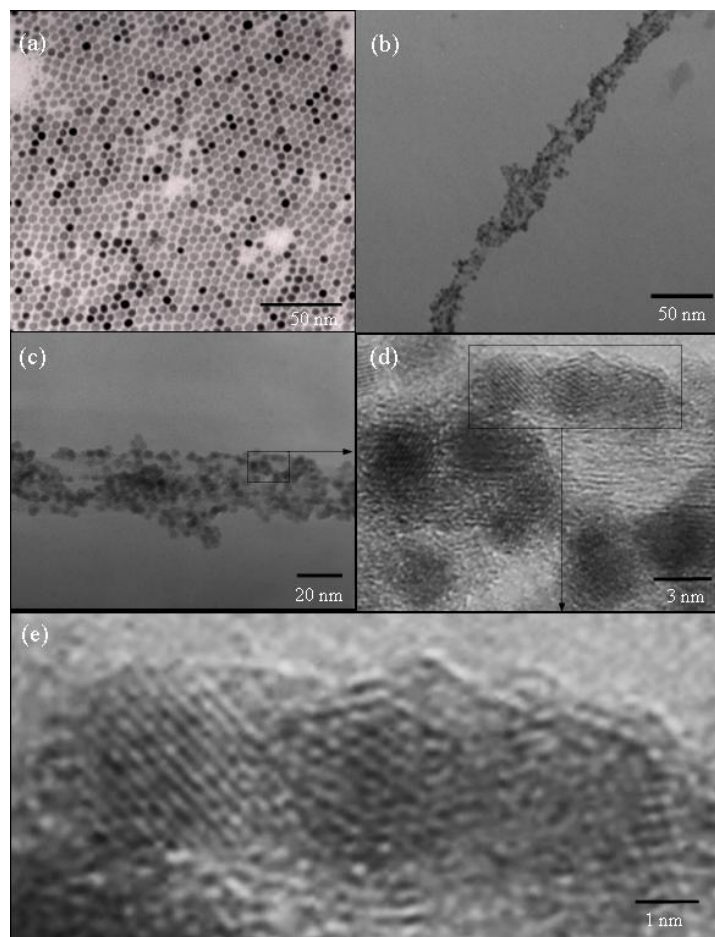


Figure 2. (a) TEM image of ~4nm PbSe QDs employed in this study. (b) TEM image of SWNT-PbSe. (c) High Resolution TEM image (HRTEM) of SWNT-PbSe. (d) Magnified High Resolution TEM image of square area in Fig. 2c. (e) Magnified High Resolution TEM image of square area in Fig. 2d.

Composite dispersion of the constituents was performed by combining appropriate proportions of PVK and SWNT-PbSe complex in chloroform, followed by homogenization via vigorous stirring and ultrasonication. A 50-nm-thick layer of PEDOT/PSS (Baytron-P, Bayer) was spin-cast on the ITO substrates to improve charge transport through the device. This is followed by spin-casting the active layer of the photodetector from the composite solution. The resulting samples (with average thickness 500-600 nm) were dried overnight in vacuum to ensure complete solvent removal. Finally, aluminum counter-electrodes were

thermally evaporated through a standard shadow mask under high-vacuum to yield a sandwich device structure with active area $\sim 0.04 \text{ cm}^2$. Figure 3 shows the measured dark currents and photocurrents in two different sets of composite devices. In one set consisting of the PbSe QD/PVK composites, the photocurrent increases significantly as a function of the loading fraction of QDs. Pure PVK has negligible absorption at wavelengths longer than 370 nm and no photoresponse on 1340 nm excitation was obtained when only PVK was used. Hence, the increased photocurrent indicates quantitative infrared sensitization of the polymer by the QDs. In the other set of devices containing the SWNT-PbSe complex, the photocurrent was enhanced even further, as compared to those devices from the first set containing just the QDs., Figure 3 depicts the result with different loading wt% of the SWNT-QD conjugate in the composite. It was noted that for devices containing the SWNT-PbSe conjugate, the photocurrent is larger per effective load fraction of the PbSe QDs. For example, the photocurrent at 15 wt% loading of the SWNT-PbSe conjugate surpasses that of 20% load fractions of solitary PbSe QDs. The best performance was extracted from the devices containing 20 wt% of SWNT-PbSe conjugate. The enhancement in photocurrent, compared to devices incorporating just the QDs with equal loading of the photosensitizing QD, is more than 2 times at the highest operating bias. The dark currents are always less than 10^{-7} A , for all the measured devices. One important concern for this single active layer device is that the SWNT ropes or bundles could potentially short-circuit the electrodes along the thickness of

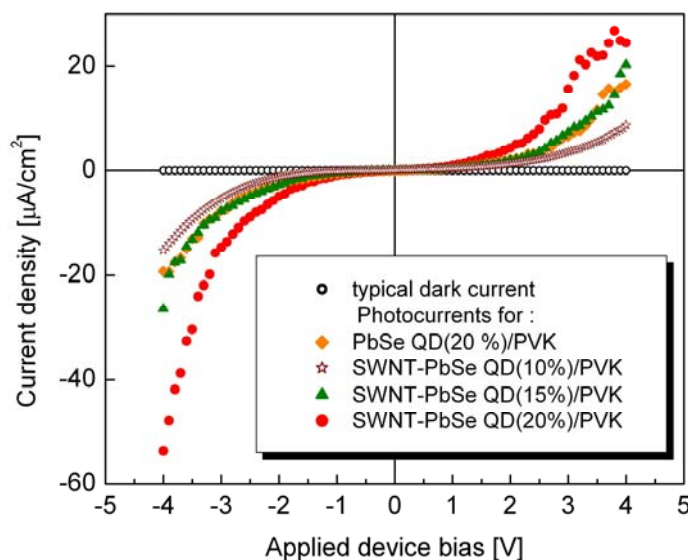


Figure 3. *I-V* characteristics of PbSe QD/PVK and SWNT-PbSe /PVK devices in dark and under illumination, illustrating the enhancement of photocurrent in the IR in devices with increasing content of the SWNT-PbSe QD conjugate.

the nanocomposite device provided (i) a single rope is longer than the thickness of the device,

(ii) many ropes form a percolative dc network across the thickness. As is observed here, the dark current remains very low even upto the highest applied bias of 4V; hence there is no incidence of SWNTs' short circuit in the nanocomposite. This may have been also assisted by the centripetal force during spin-casting that would tend to align the SWNT ropes in the plane of the substrate rather than across the thickness of the device. The orientation of the ropes would also depend on the viscosity of the cast solution, the solvent evaporation rate and the concentration of the SWNTs. All in all, it is obvious that short circuit due to SWNT in our case is not an issue. The external quantum efficiency (EQE) of such photodetectors is defined as the ratio of the number of collected charges at the electrode to the number of incident photons at the wavelength of operation. Efficient harvesting of IR photons followed by fast charge transfer and enhanced conduction in the polymer and SWNT networks results in a maximum EQE of ~2.6%, obtained in the devices with 20 wt% of SWNT-PbSe. Compared to the PbSe QD/PVK devices (with same amount of solitary QDs) that exhibit EQE of ~1.2%, this is more than 100% increment.

This study shows that by incorporating SWNT-PbSe conjugate where a copious population of PbSe QDs is attached to the nanotubes, efficient charge separation and transport is achieved. The study combines distinct merits of the constituents of a polymeric nanocomposite, namely high efficiency excitonic generation of PbSe QDs; efficient electron transfer to SWNT due to intimate and high density attachment of QDs; low percolation threshold dc conduction path due to SWNT; and above all a ballistic transport mechanism in SWNT- all of which lead to a stupendous enhancement of photocurrent over and above a device without the SWNT constituent.

3.1. System II

We have developed new synthetic pathways for easy access to rigid C₆₀-tethered 2,5-dithienylpyrrole triads (Figure 4). The π -conjugated 2,5-pyrrole moieties were chosen both as photo-excited electron donor segment and light absorbing chromophore, whereas the C₆₀ acts as an acceptor. The phenyl moiety was chosen to provide a rigid framework in the molecular structure for forming a stable and conducting footing in SAM. As we expected, the use of more electron-rich 2,5-pyrrole segment resulted further extend the lifetime of the charge-separated state of the system. Conjugation length of chromophore segments was extended to cover longer wavelength absorption and to increase electron density on chromophore. Moreover this strategy also contributes to enhance light absorption ability by attaching - C₆₀ at both ends of an chromophore to prevent C₆₀s from blocking the chromophore core so that more light can be absorbed by the chromophore. In this structure, C₆₀s and the chromophore are spatially separated; apart which increases the molecule's efficiency in light harvesting.

This work is being prepared to be published.

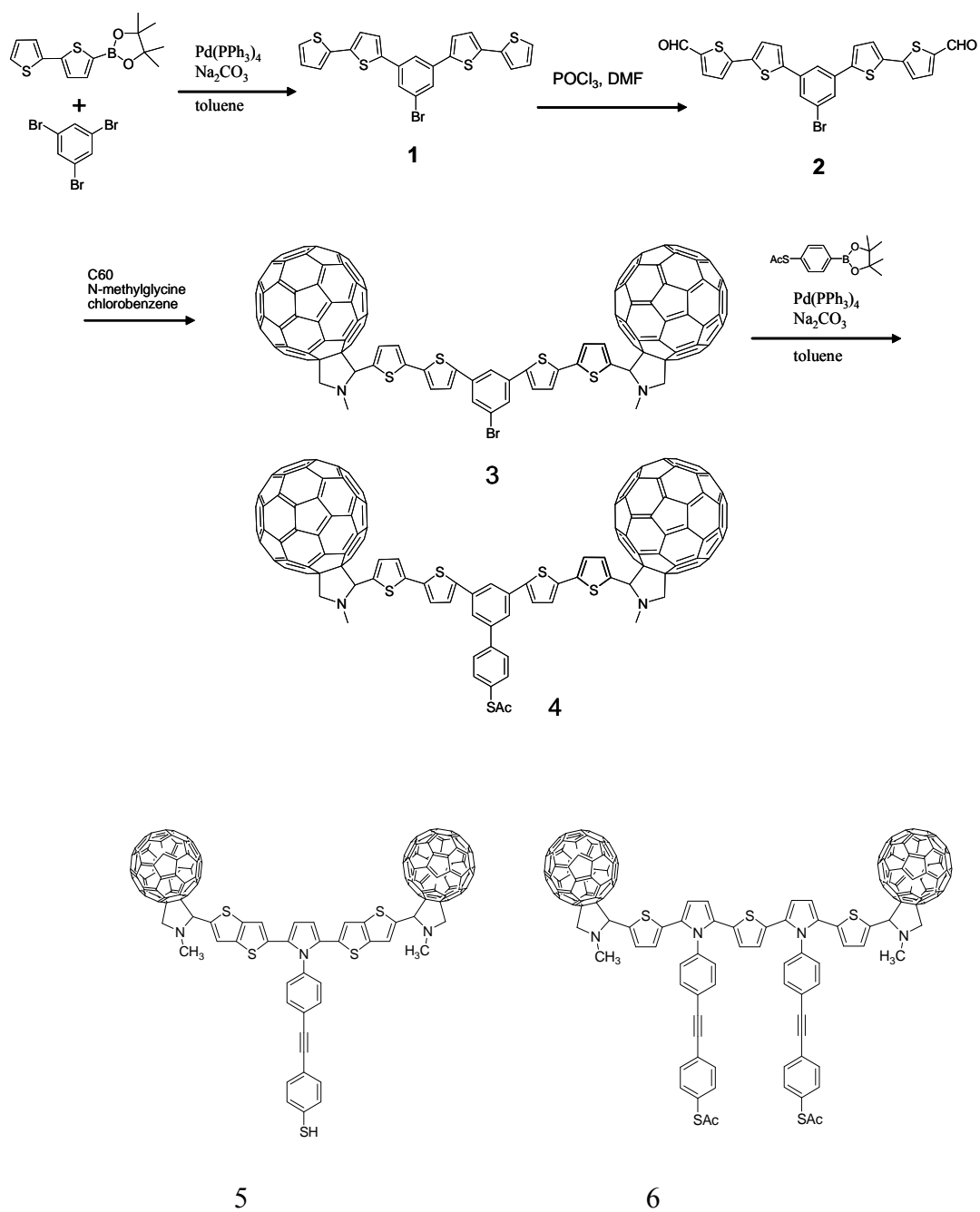


Figure 4. Proposed C₆₀-tethered 2,5-dipyrrole triads with extended π -conjugation

4. Publication and Conference Presentation

Publication:

1. N. C. Cho, K. R. Choudhury, R. B. Thapa, Y. Sahoo, T. Ohulchanskyy, A. N. Cartwright, **K.-S. Lee**, and P. N. Prasad, *Adv. Mater.* 19, 232-236 (2007)

"Efficient photodetection at IR wavelengths by incorporation of PbSe-carbon nanotube conjugates in a polymeric nanocomposite" (Appendix 1)

⇒ ***This paper was highlighted as a "Heart Cut" paper***

by the American Chemical Society (Appendix 2)

2. N. C. Cho, K.-S. Kim and K.-S. Lee, in preparation

"Self-Assembled C₆₀-Based Photofunctional Materials with Enhanced Photocurrent Density"

Conference Presentation:

1. N. C. Cho, K. R. Choudhury, R. B. Thapa, Y. Sahoo, T. Ohulchanskyy, A. N. Cartwright, P. N. Prasad and **K.-S. Lee**, "Efficient Photodetection by Incorporation of PbSe/Single-Walled Carbon Nanotube Conjugate with Conducting Polymer at IR Wavelength", *The 17th Symposium on Molecular Electronics and Devices*, Hanyang Univ. Seoul, Korea, June 10-13, 2006.

2. **K.-S. Lee**, "Nanoscale Ordering of Functional Materials by Guided Self-Assembly for Photovoltaic Application: Synthesis and Characterization", *3rd US-Korea Workshop on Nanoelectronics*, UCLA, Los Angeles, USA, August 8-9, 2006.

3. **N. C. Cho**, K. R. Choudhury, Y. Sahoo, T. Ohulchanskyy, P. N. Prasad and K.-S. Lee, "Efficient Photodetection at Infrared Wavelengths by Incorporation of PbSe/Carbon nanotube Conjugate in a Polymeric Nanocomposite", *Korea-Japan Joint Forum 2006*, Niigata, Japan, October 2-5, 2006.

4. N. C. Cho, K. R. Choudhury, Y. Sahoo, T. Ohulchanskyy, P. N. Prasad and **K.-S. Lee**, "Incorporation of PbSe/Single-Walled Carbon Nanotube Composite with Conducting Polymer for Efficient Photodetection at IR Wavelength", *IUPAC International Symposium on Advanced Polymers for Emerging Technologies/2006 PSK Annual Fall Scientific Meeting*, Busan, Korea, October 10-13, 2006.

5. **K.-S. Lee**, "Pentacene-Quantum Dot Polymeric Nanocomposite for Infrared Photodetection", *SPIE Photonics WEST*, San Jose, California USA, January 20-25, 2007.

(Representative File of Conference Presentation is in Appendix 3)

Appendix 1

Publication: *Adv. Mater.* **19**, 232-236 (2007)

Appendix 2

**Highlighted as a “Heart Cut” Paper
by American Chemical Society**

Appendix 3

Representative File of Conference Presentation